

# Survivability of Affordable High Temperature Polymer Matrix Composites for Propulsion Engine Components

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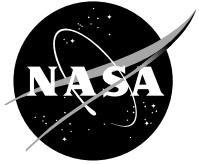
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## **Abstract**

PMR-type polyimides are regarded as state of the art high temperature polymers, due to their excellent thermo-mechanical properties and thermo-oxidative stability. One of their drawbacks, however is the inability to process them using cost-effective processing methods such as Resin Transfer Molding (RTM) and Resin Film Infusion (RFI). Development of low viscosity, high temperature polymers has been the subject of intense research. Recently, a new generation of low viscosity polyimides were synthesized by the introduction of twisted biphenyl or binaphthyl groups into the backbone.<sup>1</sup>

This report details the progress for Year 1, which has involved acquiring samples and initiating Phases I and II of the proposed research. Specifically, studies of the process-property relationships of a series of polymers using oligomers based on 2,3,3', 4'-biphenyltertracarboxylic dianhydride (PBDA) and a mixture of a diamine, BAX and a triamine, 1,3,5-Tris (4-aminophenoxybenzene), TAB, where the amount of TAB was varied have been initiated. The sample containing 10% Tab possesses a slightly higher degree of crystalline order versus that of the 20% TAB sample, based on x-ray diffraction studies of the b-staged oligomers. Both systems lose all of the crystalline order upon curing, however. The chemorheology has been studied as a function of the TAB content. While the magnitude of the viscosity is essentially the same for both systems, the cure kinetics of the 10% TAB system is faster than that for the 20% TAB system. The sample exhibits a melting-recrystallization-remelting behavior before the crosslinking commences. Correlation of other kinetic parameters, such as the activation energies for curing, the T<sub>g</sub> and mechanical properties to the structure of these systems is underway. Future studies will involve characterization of mechanical and thermal properties of the pure resins and the fabrication of fiber reinforced composites using these materials.

## **Introduction**

The object of this research is to develop cost effective fiber reinforced composite manufacturing processes such as Resin Transfer Molding (RTM) and Resin Film Infusion (RFI) and evaluate their high temperature properties. The study utilizes a series of these polymers using oligomers based on 2,3,3', 4'-biphenyltertracarboxylic dianhydride (PBDA) and a mixture of a diamine, BAX and a triamine, 1,3,5-Tris (4-aminophenoxybenzene), TAB, where the amount of TAB was varied.

This report describes activities and progress associated with two phases of the research: I. Process-Property Studies of the Pure Resin and II. Utilization of VARTM to fabricate fiber reinforced composites.

## Report on Progress

Initiation of the project was hampered due to nonavailability of samples. However, small amounts of samples (ca. 30 grams) were supplied by Sandi Campbell of the Polymers Branch of the Glenn Research Center in August 2002. These quantities enabled the initiation of Phase I research, which involves studies of the chemorheological behavior.

Differential Scanning Calorimetry (DSC) was performed to determine the thermal transitions in the samples denoted as TAB 10 or TAB 20, corresponding to the percentage of the Tab monomer incorporated. As shown in Fig. 1, the DSC scan exhibits a large endotherm at 175°C, due to monomer melting. Two smaller endotherms are visible at 210 and 220°C, followed by a smaller, broader endotherm at ca. 250°C. The development of these resins allows studies of the flow behavior (i.e. melt viscosity) and chemorheology which were not possible with PMR-15. Parallel plate rheology was done to characterize the flow and curing behavior. A plot of the resin viscosity versus temperature for samples containing 10 and 20%, TAB, respectively, is shown in Fig. 2(a). This experiment was done by choosing a temperature that was above the largest endotherm observed in the DSC curve and that was high enough to enable the sample to flow and cover the entire plate. Thus the initial temperature is 225°C. As the temperature increases, the viscosity steadily decreases to a minimum at ca. 300°C. After this minimum, the crosslinking initiates, leading to a sharp increase in the viscosity up to ca. 340°C, after which the viscosity reaches a plateau, indicative of complete cure. The crosslinking initiation occurs faster in the sample containing 10% TAB. A better view of the viscoelastic behavior of these systems is gained by plotting the storage modulus,  $G'$  versus temperature as shown in Fig. 2(b). These curves reveal an initial minimum at ca. 230°C, followed by a slight but reproducible increase in the modulus up to ca. 385°C, followed by a larger drop before the crosslinking is initiated. The modulus increase after the initial minima is presumed to be due to crystallization, after the initial melting.

Based on the above experiments, several isothermal temperatures were selected to study the isothermal curing behavior rheologically. An isothermal curve obtained at 270°C for sample containing 20% TAB is shown in Fig. 3(a). Both the storage modulus, and the loss modulus,  $G''$  are plotted. The point at which the two curves intersect is widely defined as the gel point,  $t_{gel}$ , of the system. The  $t_{gel}$  for this temperature is 1500 sec. A plot of the extent of cure (determined by infrared spectroscopy) versus time at this temperature shows that the degree of cure at 1500 seconds is ca. 80% (Fig. 4). As the temperature is increased, the gel time decreases (Fig. 3(a) to (c)). Studies have only been conducted for the 20% TAB sample, due to lack of 10% TAB. Future studies will involve determination of the activation energies associated with curing for these systems.

The morphology of the polymer before and after cure, Fig. 5, shows that the oligomer is crystalline, but all order is lost after crosslinking occurs. Thermal ( $T_g$ , decomposition) and mechanical properties (modulus, strength, toughness) will be evaluated during the next month.

A high temperature VARTM cell has been developed. In addition, high temperature compression (IITRI-ASTM D3410.25) and bend fixture (ASTM D2344.10) have been acquired and a high temperature test facility (1000 °C) with MTS TestStar IIs controller has been installed.

Dr. Mike Meador of the Polymers Branch, Glenn Research Center will supply resin in sufficient quantity to fabricate composite panels using the VARTM process. In the future, larger resin quantities will be purchased or synthesized in our laboratory.

## References

1. Meador, M., Meador M.A.B., Petkovsek, J., Oliver T., Scheiman, D., Gariepy, C., Nguyen, B., Cby, R.K., Proceedings of XXI High Temple Conference, St. Petersburgh, FL, 2001.

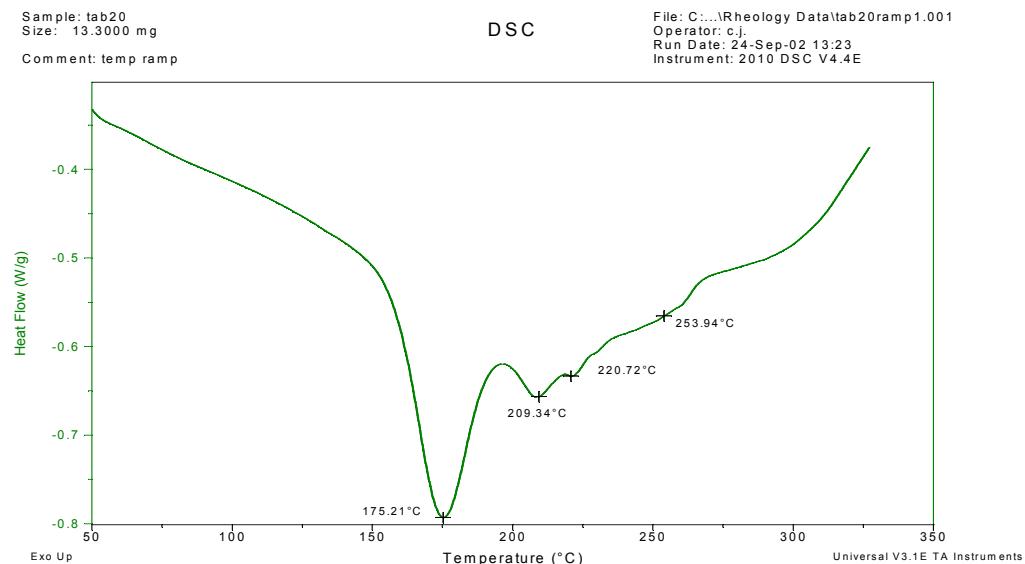


Figure 1. DSC scan of uncured oligomer containing 20% TAB.

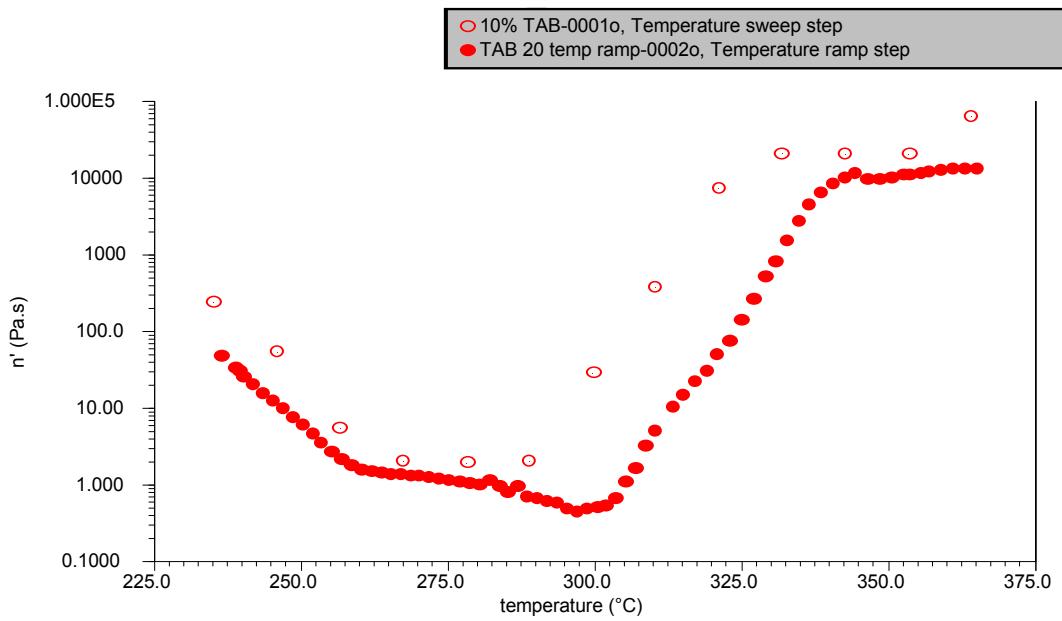


Figure 2(a). Viscosity versus temperature for uncured oligomers containing 10 and 20% TAB.

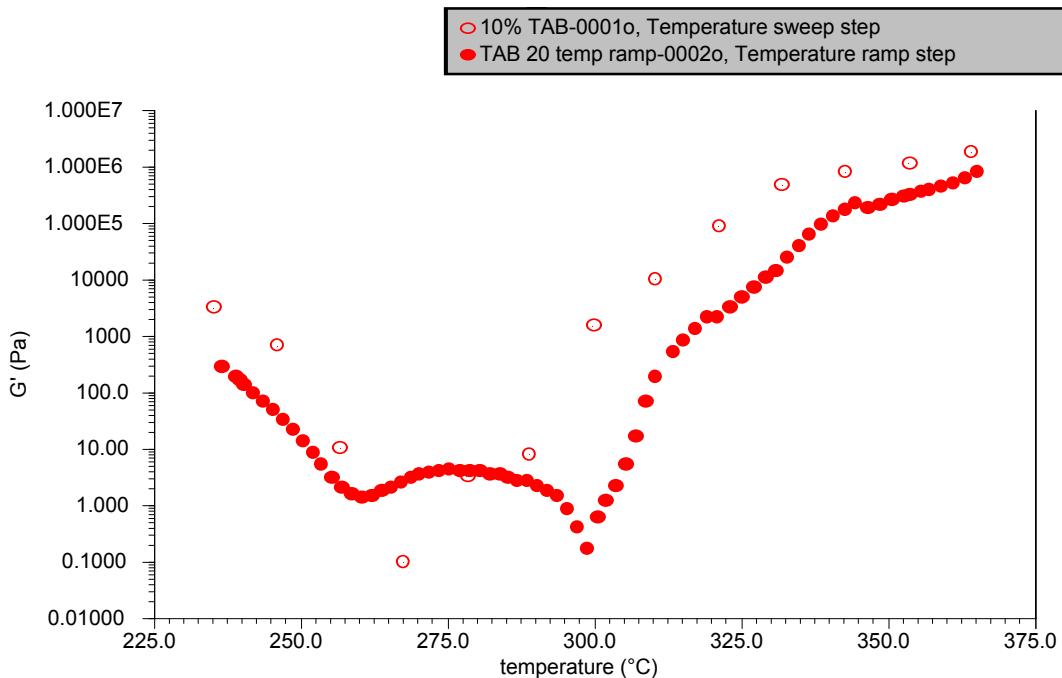


Figure 2(b). Storage Modulus versus temperature for uncured oligomers containing 10 and 20% TAB.

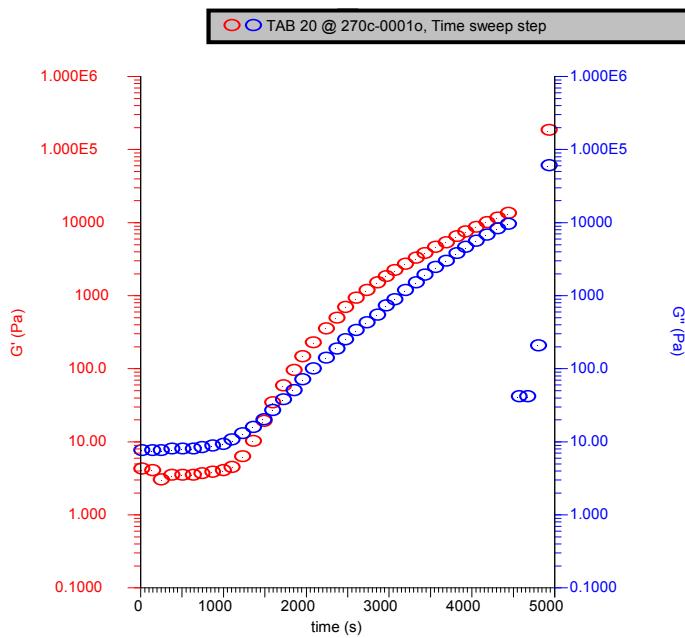


Figure 3(a). Time sweep at 270°C for uncured oligomer containing 20% TAB.

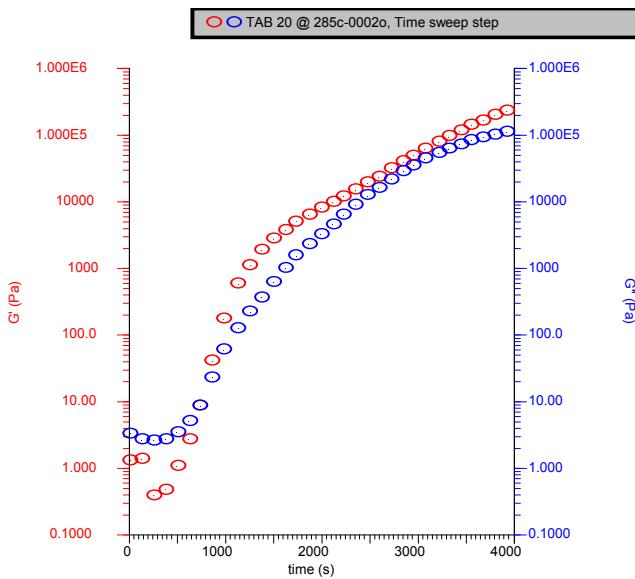


Figure 3(b). Time sweep at 285°C for uncured oligomer containing 20% TAB.

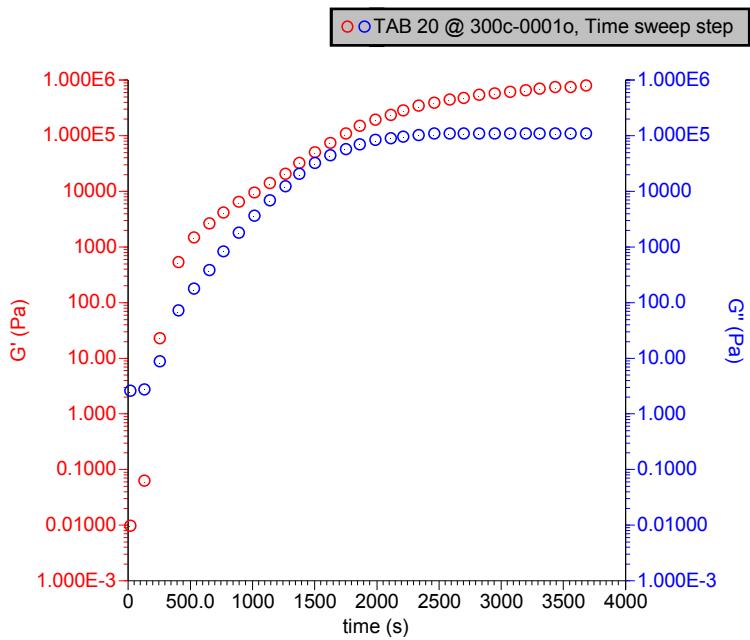


Figure 3(c). Time sweep at 300°C for uncured oligomer containing 20% TAB.

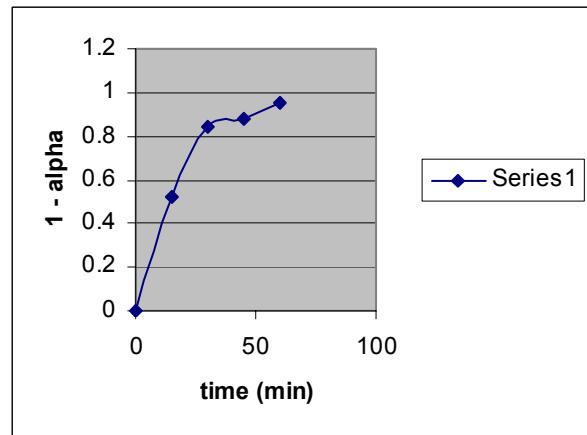


Figure 4. Extent of cure at 270 °C for uncured oligomer containing 20% TAB.

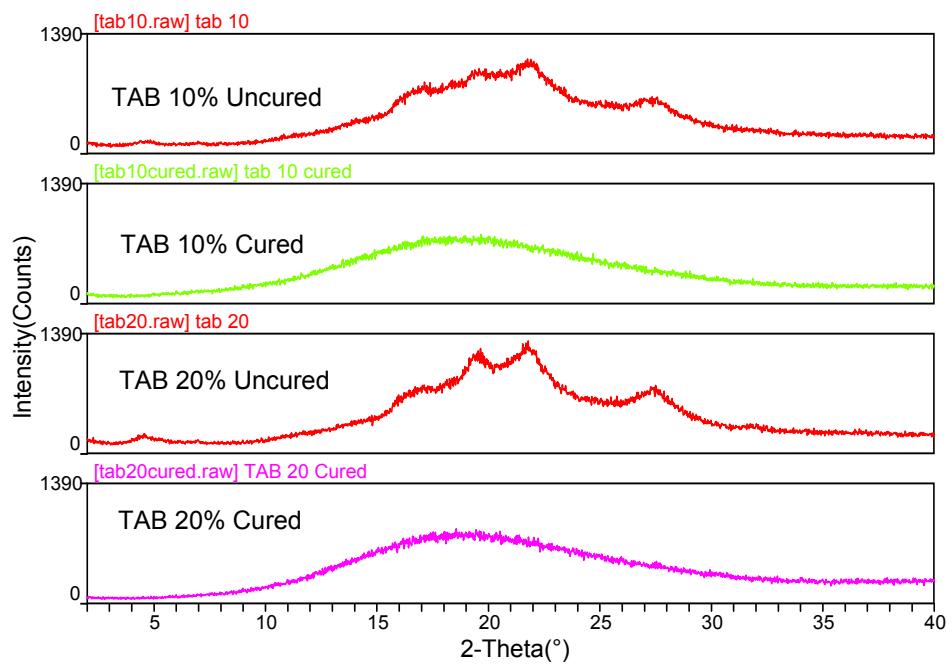


Figure 5. X-ray diffraction scans for uncured oligomers and cured polymers containing 10 and 20% TAB.

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